



Effect of a thin ceramic-coating layer on thermal and electrochemical properties of polyethylene separator for lithium-ion batteries



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HIGHLIGHTS

- CMC–SBR is used as mixed binder to prepare ceramic-coating separator.
- Only 5% in weight of CMC–SBR is needed to form the coating slurry.
- The solvent water is environment friendly.
- Punch cells with ceramic-coating separator present excellent properties.

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ABSTRACT

In this paper, a new kind of ceramic-coating separator for lithium-ion batteries is successfully prepared by forming a ceramic layer consisted of Al_2O_3 powder, carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) mix binder onto one side of pristine PE separator. During the preparation of the separator, water is used as solvent and a very small amount of SBR–CMC mixture is applied as binder to obtain better thermal stability. The effect of thickness of the ceramic-coating layer on its thermal stability, physical properties and electrochemical performance is also investigated. The results clearly showed that the ceramic-coating separator with SBR–CMC binder has wonderful thermal stability, good wettability and high uptake of liquid electrolyte. Pouch cell tests with the ceramic-coating separator also show excellent stable cycle performance.

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1. Introduction

Lithium-ion batteries have been widely used in portable consumer electronics due to the high energy density and particularly good cycle life [1]. Furthermore, lithium-ion batteries are also regarded as one of the most promising power sources for electric vehicles (EVs) and storage of new energy in a smart grid [2]. In most commercialized lithium-ion batteries, polyolefin porous membranes, specifically polyethylene (PE) and polypropylene (PP), have been used as separators which prevent physical contact of the positive and negative electrodes while permitting free ionic transport within the cell. Although such membranes offer some

advantages as excellent mechanical strength and chemical stability, they exhibit large thermal shrinkage at high temperature [3], which could cause a short circuit between electrodes in cases of some inevitable occurrence of hazardous behaviors, such as electrical overcharging and high thermal impact. This shrinkage and resulted short circuit usually induces the thermal runaway of LIBs, which could eventually lead to fire or explosion of the cells. A shutdown separator composed by multilayer polyolefin as PP/PE/PP is commonly used as a fail-safe device in commercial cells to prevent this problem [4]. Multilayer separators offer advantages by combining the lower melting temperature of PE with the high-temperature strength of PP. As the temperature approaches the melting point of PE (~130 °C), the porosity in the separator collapses, so that cells fail as the ion conduction is cut off. But if the temperature continues to increasing above the melting point of PP (~160 °C), the separator could fail in separating the electrodes, thereby result in internal shorting of the cell potentially [5].

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Therefore, a separator that does not shrink or melt at elevated temperatures becomes desirable.

The application of composite separators, which are prepared by using binders to coating the organic materials, inorganic materials or organic-inorganic mix materials on the surface of the polyolefin separators, is an effective method for improving the safe performance of the LIBs [6–10]. Among them, the ceramic-coating separator draws considerable attention as it combined characteristics of polymeric separator and heat resistant inorganic powder. Al_2O_3 [9,11,12] and SiO_2 [13,14] were usually used as the inorganic powder, while polymethyl methacrylate (PMMA) [6], polyvinylidene fluoride (PVDF) [12], polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) [13,14] and other polymers [11] were used as the binder in ceramic-coating separator. However, such binders cannot meet the requirement for safety of the battery due to their high shrinkage. In addition, most binders are readily swollen, gelled, or even dissolved in non-aqueous liquid electrolytes to form viscous fluid or gel polymer electrolyte, which results in desquamation of coating layer from the separator [15]. Furthermore, those binders were usually consumed more than 20% in weight to form the coating layer [9,11].

In this paper, a kind of ceramic-coating separator (CCS) for lithium-ion battery was developed. Al_2O_3 and PE separator and a water-soluble binder composed of carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR) were applied as the coating substrate, inorganic powder and binder respectively. SBR–CMC mixture binder is not only a high adhesion agent but also a strong dispersion medium [16,17], which favors the uniform distribution of Al_2O_3 particle. Compared to other polymer binders such as PVDF, only 5% in weight of SBR–CMC is needed to form the coating slurry and as the solvent, water is friendly for environment. The effect of thickness of the ceramic-coating layer was also carefully studied. The CCS membrane with SBR–CMC binder shows wonderful thermal stability, better wettability and higher uptake of liquid electrolyte. Pouch cell tests with CCS membrane also show better stable cycle performance.

2. Experiments

2.1. Preparation of the ceramic coating separators

The slurry for ceramic-coating layer was prepared by mixing Al_2O_3 particle (Average particle size = 400 nm, Taimei Chemicals, Japan), SBR and CMC (Guangzhou Songbai Chemical, China) into water/ethanol (5 ml: 5 ml) mixed solvent, where the weight of Al_2O_3 /SBR/CMC was fixed at 0.95 g/0.03 g/0.02 g. After ultrasonically dispersed for 10 min, the slurry was further subjected to vigorous mixing by bead-milling with a speed of 400 r min^{−1} for 2 h. A PE separator (thickness = 20 μm, Asahi Kasei, Japan) manufactured by a wet process was chosen as the coating substrate while the coating slurry was applied onto one side of the pristine PE separator by automatic film coating machine (Shanghai Environmental Engineering Technology Co., Ltd, China). The thickness of the coating layer can be accurately controlled by the slit of the applicator. After the coating process, the prepared separator was dried under vacuum line at 60 °C for 6 h to remove the solvent in the coating slurry. The CCS membrane with the coating layer controlled in 3 μm, 6 μm, 9 μm were respectively prepared and referred to as CCS-3, CCS-6 and CCS-9 membrane.

2.2. Electrode preparation and cell assembly

The battery performance of the material was tested using pouch cells (7.5 cm × 3 cm × 0.3 cm, 280 mAh). The cathode had a composition of 90wt. % LiCoO_2 (Hunan Shanshan New Material Co.,

China); 5 wt. % Super-P, 5 wt. % PVDF and anode had a composition of 95 wt. % synthetic graphite (Shanghai Shanshan New Material Co., China) and 5 wt. % PVDF. The *N*-methyl pyrrolidine (NMP)-based cathode slurry was coated on a 15 μm thickness aluminum foil and anode slurry was coated on a 10 μm thickness copper foil then dried at 80 °C overnight in a vacuum drying oven. The prepared CCS membrane and pristine PE separator used as pouch cell's separator, the pristine separator used as reference. The pouch cell was injected the same weight of electrolyte. All cells were assembled in a glove box (Mbraun, Germany) filled with argon gas.

2.3. Characterization of the ceramic coating separators

The surface and cross-sectional morphologies of the pristine PE separator and CCS membranes were investigated by using a field emissions scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan), while the membranes were cooled in liquid nitrogen and broken into two parts mechanically, and then the SEM micrographs of the cross-sections were taken. The thermal shrinkage of the ceramic-coating separators was determined by measuring the dimensional change (area based, 4 cm square) after being subjected to heat treatment at various temperatures for 0.5 h and the shrinkage can be computed as the following equation:

$$\text{Shrinkage}(\%) = \frac{S_0 - S}{S_0} \times 100\%$$

where S_0 and S stand for the area of separator before and after heat treated. The hot punch test was measured by putting the separator 3 mm below the automatic temperature control metal bar (200 °C and 2 mm in diameter) for 1 min. The contact angle measurement of the PE separator and CCS membranes was carried out by using a commercial drop shape analysis system (Powereach JC2000C1, Shanghai Zhongchen Digital Technique Equipment Co. Ltd., China) to ascertain the effect of the coating layer on the wettability of the electrolyte. The electrolyte uptake was computed as following equation:

$$\text{Uptake}(\%) = \frac{W - W_0}{W_0} \times 100\%$$

where W_0 is the net weight of membrane, and W is the weight of the membrane after absorbing the liquid electrolyte. The ionic conductivity of the CCS membrane with electrolyte was measured by sandwiching the membranes between two stainless steel electrodes. Impedance data were obtained with electrochemical workstation (Solartron, SI-1260, England) over a frequency range of 1 Hz–100 kHz.

Punch cells were assembled by sandwiching the separator between graphite anode and LiCoO_2 cathode, and then the liquid electrolyte was added. Before the electrochemical tests, the cell was activated by cycling it at 0.1 C rate in a voltage range of 3 V–4.2 V. The charge and discharge cycling tests of the cell were measured at 0.5 C with battery test equipment (LAND-V34, Land Electronic, China). The heating test of the LiCoO_2 /graphite punch cell which was fully charged to 4.2 V at room temperature was carried out by storing the cells in a drying oven of 130 °C to monitor its OCV changes with electrochemical workstation. To analyze the change of cell and electrode structure during the above mentioned tests, the punch cells were opened in glove box.

3. Results and discussion

The top surface scanning electron micrographs of the pristine PE and a series of CCS membranes are shown in Fig. 1. The pristine PE

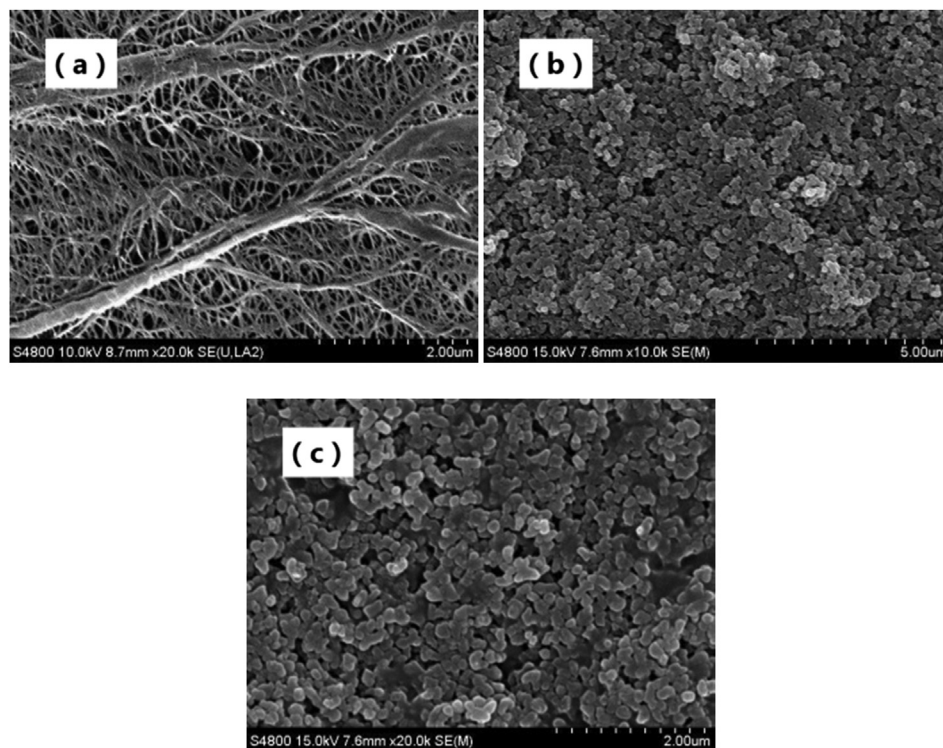


Fig. 1. Surface morphology of pristine PE separator (a) and CCS membrane (b) (c).

separator shows a typical morphology of wet process (Fig. 1a) which exhibits a uniformly interconnected submicron pore structure. In contrast to the uncoated PE separator, the CCS membranes have unique ceramic-coating layer that the fine Al_2O_3 particle connected by SBR–CMC mixed binders are homogeneously distributed in the surface layer without agglomeration of the particles. This coating layer is expected to prevent the separator from being thermally shrunk owing to the existence of heat-resistant Al_2O_3 powders so that physical contact of the cathode and the anode could be always prevented even in cases of some inevitable occurrence of hazardous behaviors. It also can be found that the exist of porous structures in the inorganic particulate layers forming by Al_2O_3 particles, which are expected to play a key role in improving the electrolyte wettability, uptake of liquid electrolyte and ionic conduction of the membranes with electrolyte. The cross-sectional morphologies of CCS-3, CCS-6 and CCS-9 membrane shown in Fig. 2 present that the thickness of the coating layer can be accurately controlled. It has been pointed out that a uniform thickness for LIBs is critical for long cycle life [3]. Therefore, the uniformity of the separators in thickness is also an important requirement and characterization for practical use.

The essential function of a separator is to prevent physical contact of the positive and negative electrodes while enabling ion to transport between the electrodes. Thus, the separators should be chemically, electrochemically and mechanically stable in the battery even at high temperature. Otherwise, the anode and cathode would contact each other and then the cell will not function with thermal runaway even combustion or explosion, especially at abused use conditions. In order to investigate the thermal-resistant characteristics of the CCS membrane, thermal shrinkage behavior is observed by measuring the dimensional change (area-based) after storing the membranes at a series of temperature from 115 °C to 145 °C for 30 min respectively. The results are shown in Fig. 3. Since conventional PE separators prepared through multiple stretching

processes have a melting point of around 130 °C, they are easily to lose the dimensional stability after exposure to high temperatures of above 110 °C. In addition, the thermal shrinkage of the CCS membranes was further examined as a function of coating thickness. At relatively low temperatures (below 135 °C), the thermal shrinkage for membranes of different coating thickness does not exhibit significant change. Thermal shrinkages of CCS-3, CCS-6 and CCS-9 membranes are about 29.3%, 12.7% and 2.5% at 145 °C. As a comparison, the pristine PE separator has a thermal shrinkage of 63.5% at that temperature. Fig. 4 shows photographs of pristine PE and CCS membranes (4 cm square) subjected to heat treatment before/after 130 °C and 145 °C for 0.5 h. At 130 °C, the CCS-3 membrane has no significant shrinkage while the pristine PE separator has already shrunk 33.1%. Once the temperature increased to 145 °C, the thermal shrinkages of CCS-3, CCS-6 and CCS-9 membranes are about 29.3%, 12.7% and 2.5% respectively, as a comparison, the thermal shrinkage of pristine PE separator is 63.5%. The photographs clearly show that PE separator suffers a high degree of dimensional change after exposure to high temperature condition. Furthermore, the shrinkage of the CCS membrane decreased clearly with the increasing of the thickness of coating layer, while CCS-9 membrane undergone the lowest degree of dimensional change. The CCS membranes have less thermal shrinkage than pristine PE separator over a wider range of temperatures. It can be concluded that the thermal stability of CCS membranes could be effectively enhanced by introducing ceramic-coating layer. This improvement of CCS membrane in thermostability can be attributed to the introduction of a large amount of Al_2O_3 particles in ceramic-coating layer and high heat resistance of SBR–CMC as mixed binder. It must be pointed out that compared with other binders such as PVDF and PMMA, the elastomeric SBR possesses higher flexibility, stronger binding force and higher heat resistance [16]. CMC has two functional groups, carboxylate anion and hydroxyl, is well-known as an effective dispersion and

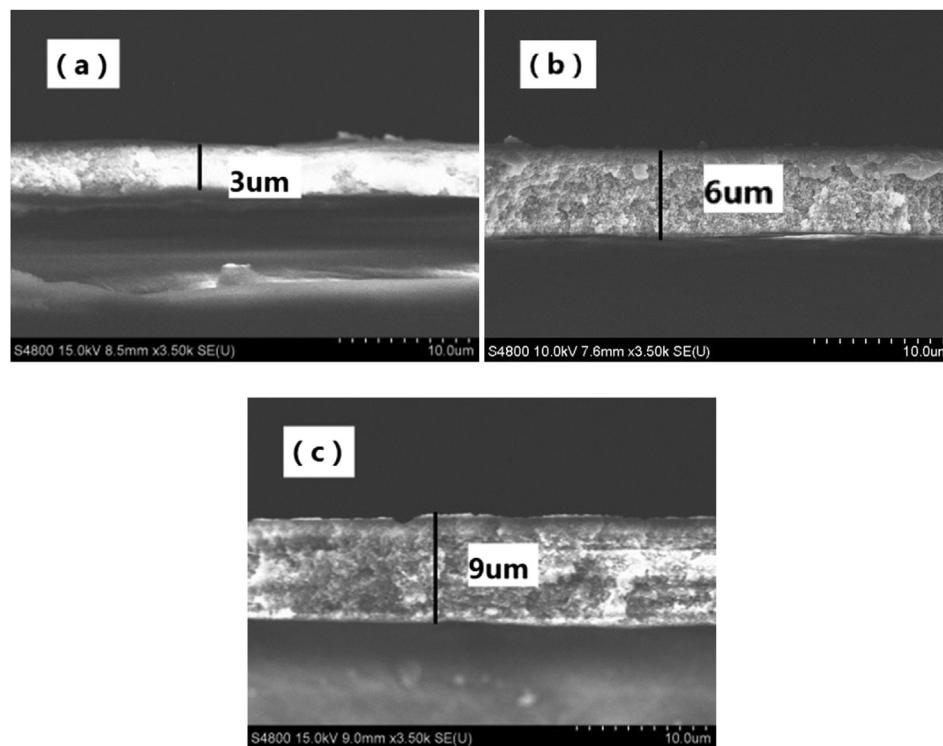


Fig. 2. Cross section morphology of CCS membranes, (a) CCS-3, (b) CCS-6 and (c) CCS-9.

thickener agent for aqueous suspension [17]. So when the mixed binder system, SBR–CMC, was used in ceramic-coating separator, better thermo-stability is obtained even in very small amounts compared with other polymer binder, for example, PMMA, PVDF and so on [9,11,18]. Furthermore, the solvent used for this mixed binder, water, is the most environmental friendly and is the least cost. It must be pointed that it is not only affordable but also beneficial for industrial production to coating ceramic slurry on the one side of pristine separator.

In order to further study the thermal stability of the membranes, a metal rod with a diameter of 2 mm was heated to 200 °C and placed at 3 mm above the PE separator and CCS-3 membrane for

1 min. It can be found that the PE membrane under the rod melted quickly and finally formed a hole, which could cause a short circuit between electrodes and induce the safety issue of the cells (Shown in Fig. 5). Although the PE substrate of CCS-3 membrane also melted down, the Al_2O_3 coating layer still remained a complete self-supporting layer to prevent physical contact of the positive and negative electrodes. This suggests that the ceramic-coating layer play a key role in preventing the separator from thermal runaway.

We also measured OCV changes of LiCoO_2 /graphite cells employing PE separator and CCS-3 membrane during heat exposure at 130 °C. The cells was fully charged to 4.2 V at room temperature. As shown in Fig. 6a, the OCV of the cells based on PE separator dropped to 0 V only after 17 min. In contrast, the cells using CCS-3 membrane was running well even after 40 min. PE separator and CCS-3 membrane in the heat-treated cell were observed and showed in Fig. 6b and c. It is easy to see that PE separator suffered a high degree of dimensional change as a result of internal short circuits of the punch cell after exposed at 130 °C, but the shrinkage is not obvious for CCS-3 membrane at the same condition. Clearly, the OCV drop of the cell using PE separator could be explained by the thermal shrinkage of the separator that causes internal short circuits in the punch cell. It seems that the better thermal stability of CCS membrane would play an important role in improving the elevated temperature characteristics of lithium-ion battery. Taking into account inflame retarding properties and safety characteristic, CCS membrane is a promising separator for lithium-ion battery even at elevated temperature.

The wettability of the separator plays an important role in battery performance because the separator with good wettability can effectively retain the electrolyte solution and facilitate ion transport between electrodes [10]. The contact angle of the electrolyte on the separator is one of the indicators for the wettability of the separator. Fig. 6 shows the images of contact angle for PE separator and CCS membrane prepared in this study. As per the usual procedure, a drop of electrolyte was deposited on the surface

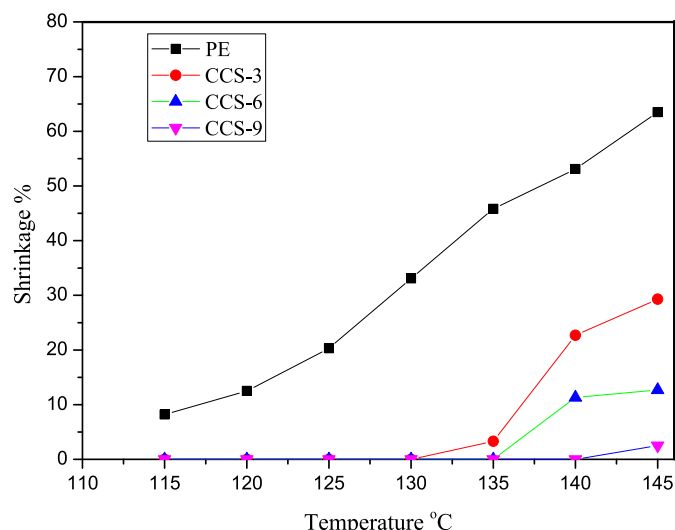


Fig. 3. Thermal shrinkage (%) of PE separator and CCS membrane.

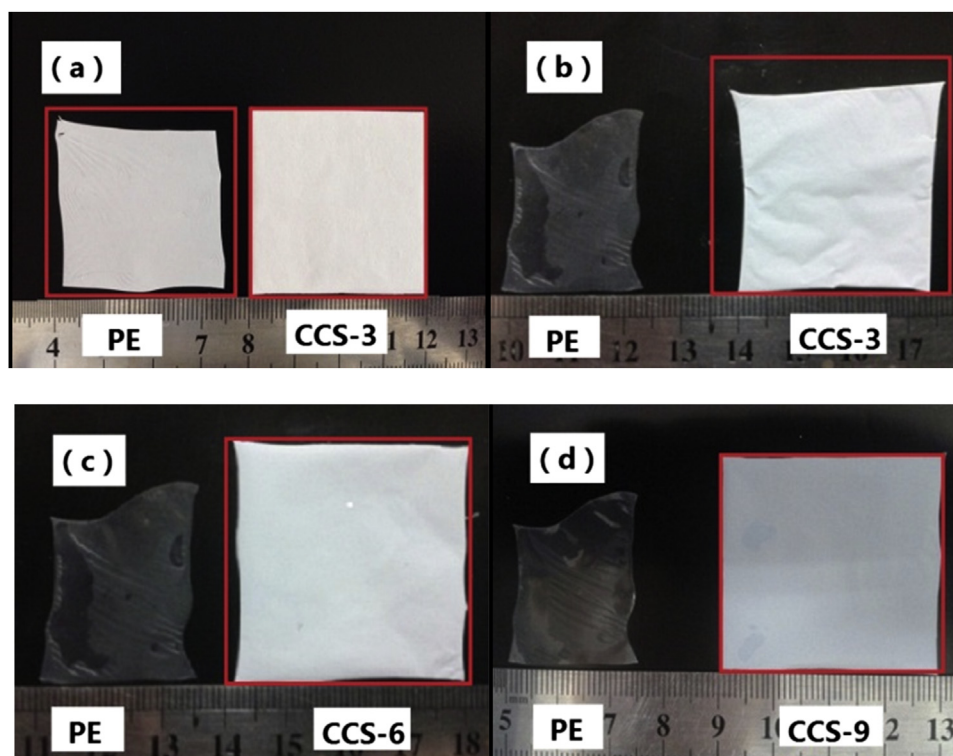


Fig. 4. Thermal shrinkage (%) of PE separator and CCS membrane at high temperature for 0.5 h. (a) PE separator and CCS-3 membrane at 130 °C. (b) PE separator and CCS-3 membrane at 145 °C. (c) PE separator and CCS-6 membrane at 145 °C. (d) PE separator and CCS-9 membrane at 145 °C.

of the separator, and the contact angle was immediately measured and recorded. As shown in Fig. 7, the contact angle for PE separator was measured as 35.0°. The contact angle significantly decreased to 0° for CCS membrane, indicating significant increase in the wettability of the surface of the separator with the electrolyte.

The electrolyte uptake is another important indicator for the separator. The electrolyte uptake and the ionic conductivity of a series of separators with electrolyte are summarized in Table 1. The electrolyte uptake of PE, CCS-3, CCS-6 and CCS-9 membrane is 54%, 70%, 75% and 82% respectively. It further suggests that the Al_2O_3 coating layer could improve the electrolyte retention in the separators. For the uncoated PE membrane, the electrolyte uptake was proportional to the porosity of the separator due to the electrolyte can only fill into its pores [14]. While in the case of CCS membrane, liquid electrolyte was not only trapped in the pores of the separator but also retained inside the porous coating layer comprised of the hydrophilic Al_2O_3 particles and SBR–CMC mixed binder. On the other hand, it can be concluded that the thicker the coating layer is, the higher the electrolyte uptake is.

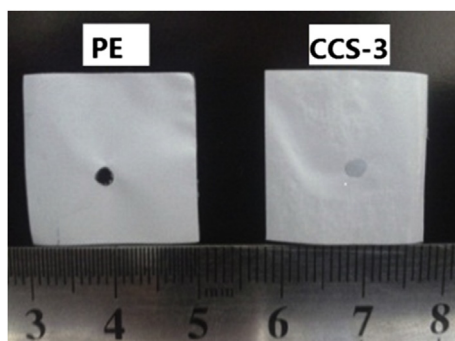


Fig. 5. Hot mental rod piercing.

Ionic conductivity of CCS-3, CCS-6 and CCS-9 membrane after soaking in electrolyte solution is 1.13 mS cm^{-1} , 1.10 mS cm^{-1} and 1.00 mS cm^{-1} at 30 °C. Ionic conductivity of CCS membrane with electrolyte is slightly decreased with increasing thickness of coating layer due to that the additional coating layer on porous PE membrane may have increased resistance of ion migration in separator. However, ionic conductivity of CCS-3 membrane with electrolyte is almost twice as that of PE separator. As the wettability increases with the coating layer, a higher uptake of the liquid electrolyte is obtained as mentioned above. It means that there are more lithium-ions in the same volume available for conduction. Furthermore, it can be concluded from a number of reports available on composite polymer electrolyte which is almost the same as the CCS membrane in formation, once ceramic particle such as Al_2O_3 is introduced, the charge and electric field associated with the particles interact with the liquid electrolyte leading to the formation of a double layer or space charge [19]. The space charge layer can promote the conduction of Li^+ [20]. This is the reason why CCS membrane with electrolyte has a higher ionic conductivity than the pristine PE separator.

Fig. 8 shows the discharge capacities as a function of cycle number (up to 50 cycles) of the cell with CCS membrane and pristine PE separator. At a charge/discharge condition of 0.5 C/0.5 C in the voltage range of 3.0 V–4.2 V, the cycling performances of both punch cells are stable. Discharge capacity of the punch cell using PE separator remains 92.4% of its initial capacity after 50 cycles and the CCS cell remains 94.7% of its initial capacity after the same cycles. This indicates that performance of lithium-ion battery using CCS membrane and PE separator is almost at the same level, meaning presence of an additional coating layer on the porous PE membrane has no evident effect on the battery performance. Furthermore, the capacity retention of cell with CCS membrane is a little higher than that of PE separator. It is thought that the ability of retain electrolyte solution in particles voids and on the Al_2O_3

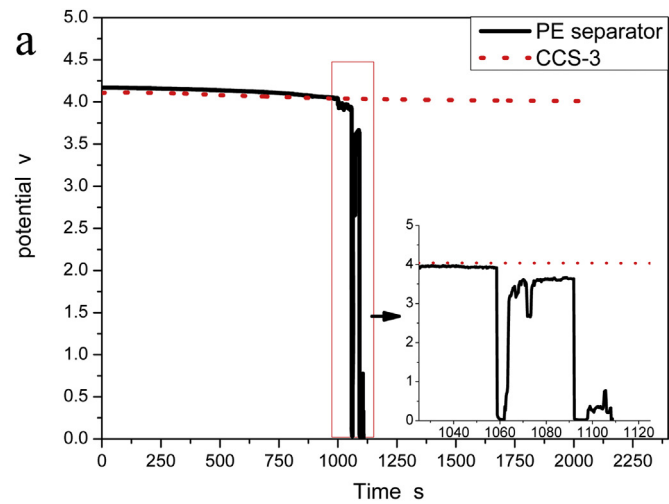


Fig. 6. (a) OCV changes of LiCoO₂/graphite cells employing PE separator and CCS-3 membrane were measured during heat exposure at 130 °C, (b) PE separator after the measurement of OCV, (c) CCS-3 membrane after the measurement of OCV.

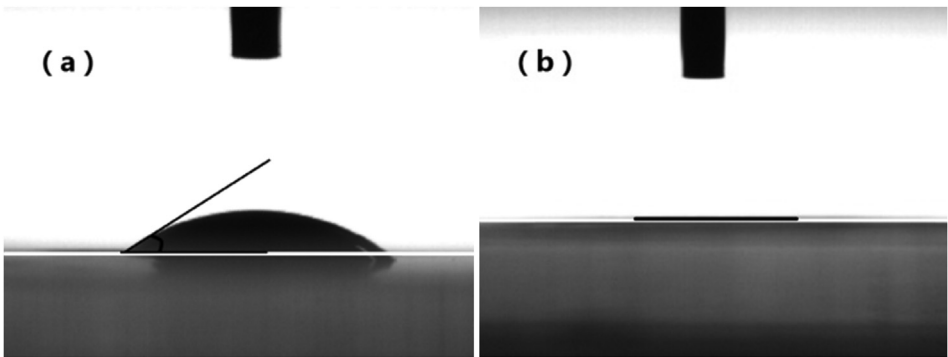


Fig. 7. Contact angle for PE separator and CCS membrane. (a) PE separator and (b) CCS-3 membrane.

powder surface of the CCS membrane is higher than that in the hydrophobic PE membrane, and thus improve the mobility of electrolyte in the separator during repeated cycling. Furthermore, Al₂O₃ can capture the trace amounts of moisture and acidic

impurity in electrolyte. Therefore the capacity retention is improved by introducing the Al₂O₃ coating layer.

Rate performance of the LiCoO₂/graphite punch cell with CCS and PE separator is also evaluated. Cells were charged to 4.2 V and discharged to 3 V at current rates of 0.5C, 1.0C and 2.0 C (Fig. 9). The results show that the capacity retention to 0.5C decreased gradually with increasing discharge rate of current. Notably, cells with CCS membrane shows better rate performance than that of PE separator at large current rate (2.0C), which can be also attributed to the higher uptake of electrolyte as well as the better wettability with liquid electrolyte, as these factors may allow for facile lithium-ion transport and good electrolyte retention during cycling.

Table 1
Physical properties of PE separator and CCS membrane.

Separator	PE separator	CCS-3	CCS-6	CCS-9
Electrolyte uptake (%)	54	70	75	82
AC impedance in electrolyte (mS cm ⁻¹)	0.78	1.12	1.10	1.00

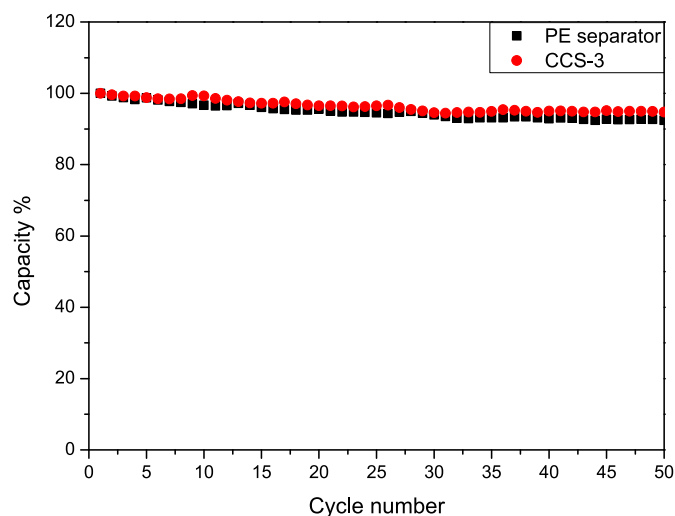


Fig. 8. Cycle performances of the battery with PE separator and CCS-3 membrane. The batteries were cycle at 0.5C for 50 cycles.

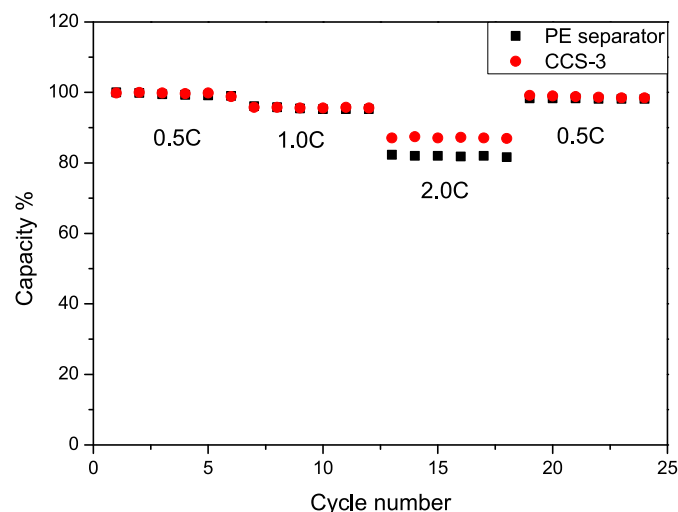


Fig. 9. Rate performances of the battery with PE separator and the battery with CCS-3 membrane at room temperature.

4. Conclusions

A new kind of ceramic-coating separator, CCS membrane is successfully prepared. The CCS membrane provides a substantial improvement in the thermal shrinkage, liquid electrolyte wettability and uptake of electrolyte. As for the CCS membrane, the uptake of liquid electrolyte become higher and the thermal shrinkage decrease with the ceramic-coating layer increasing. The punch cells assembled with the ceramic-coating separators exhibit better cycling performance than that with a pristine PE separator. Since a very small amount of binder is needed and the solvent is water, the CCS membrane is suitable for applications in secondary lithium batteries.

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